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Results for runs conducted on mixtures containing combinations of primary, secondary, and tertiary amines indicated that separate current peaks were not obtained for the various amines. Instead, a composite peak was obtained for any given mixture. Results for sulfides using a platinum electrode indicated that allyl sulfide, n-butyl sulfide and tert-butylsulfide could be oxidized in acetonitrile solution with 0.1 M $NaClO_4$ as supporting electrolyte. The order was: tert-butysulfide > n-butylsulfide > allysulfide. When amines and sulfides were mixed, a clear separation of the peaks was observed. The results indicate that it is possible to characterize a mixture of amines and sulfides by linear potential sweep cyclic voltammetry.

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ABSTRACT

Oxidation of odorous vapors at the anode of an electrochemical cell was studied as a promising approach to achieving instrumental analysis of odors.

The technique of linear potential sweep cyclic voltammetry was used to investigate the oxidizability of several amines, sulfides, and their mixtures on platinum, gold, glassy-carbon, carbon paste, and graphite electrodes. Results of the analyses of individual amines showed that the ease of oxidation on a platinum electrode in acetonitrile containing $NaClO_4$ as supporting electrolyte was: tertiary > secondary > primary.

Results for runs conducted on mixtures containing combinations of primary, secondary, and tertiary amines indicated that separate current peaks were not obtained for the various amines. Instead, a composite peak was obtained for any given mixture. Results for sulfides using a platinum electrode indicated that allyl sulfide, n-butyl sulfide, and tert-butylsulfide could be oxidized in acetonitrile solution with 0.1 M $NaClO_4$ as supporting electrolyte. The order was: tert-butylsulfide > n-butylsulfide > allylsulfide. When amines and sulfides were mixed, a clear separation of the peaks was observed. The results indicate that it is possible to characterize a mixture of amines and sulfides by linear potential sweep cyclic voltammetry. Oxidation of sulfides and amines on gold, glassy-carbon, and graphite electrodes did not reveal any significant advantage over a platinum electrode. However, a carbon-paste electrode was superior to platinum in the oxidation of sulfides.

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SYMBOLS

A	Area (cm^2)
α	Transfer coefficient
C^b	Bulk concentration
C_{ox}	Bulk concentration of the oxidized species
D	Diffusion coefficient (cm^2/sec)
D_{ox}	Diffusion coefficient of the oxidized species
$erfc(x)$	Error function complement of x
E_w	Working electrode potential
F	Faraday's Constant (96,490 coulombs/equivalent)
i	Current (amp or μamp)
i_d	Diffusion current
k_a, k_c	Rate constant for anodic and cathodic reaction
n	Number of electrons exchanged per molecule of the electroactive species
n_a	Number of electrons exchanged in the rate-controlling step
π	3.1416
R	Gas constant
Q	Coulombs (amp-sec)
T	Temperature in °K
t	Time (sec)
t	Drop time (sec)
τ	Chronopotentiometric transition time (sec)

INTRODUCTION

Many odorous emissions to the atmosphere that engender community odor nuisances contain a large number of components. Exhausts from rendering plants or diesel engines, for example, are so complex that it has not been possible to obtain sufficient analytical information to be able to reproduce their odors synthetically, despite much effort. Sensory methods have therefore been most frequently used to characterize such odors [1]. The disadvantages of sensory odor evaluation are well known. The screening and training of judges, and the use of an odor panel in the field or in the laboratory, are cumbersome and time-consuming procedures, and they often yield widely scattered results.

On the other hand, the history of "mechanical noses," devices whose responses to vapors purport to simulate human olfaction, has been disappointing; nothing comparable to a light-meter or a decibel meter has ever been developed. Since the transducing mechanism in olfaction has yet to be worked out, this circumstance is not surprising. However, any convenient instrumental method of odor measurement that would offer reasonable correlation with sensory properties would be of great help in monitoring the dispersal of odors in the outdoor atmosphere and in rationalizing the design of control systems.

To this end, we have been interested for some time in various measures of the specific oxidizability of odorous effluents. Various ambient temperature oxidation systems have, in fact, been used for odor control, such as ozonization, chlorination, and permanganate oxidation. Experience with these systems has shown that many of the most highly odorous compounds, such as mercaptans and amines, are the most easily oxidizable. The circumstances are complex, because various alternate reaction pathways may be involved, but in most sequences the change in odor with progressive degrees of oxidation is very drastic.

On various theoretical and practical grounds, we have assumed that the most promising approach to achieving instrumental analysis of odors at this stage of our knowledge about olfaction would be oxidation at the anode of an electrochemical cell. A number of relatively new and highly discriminating techniques[2] have been developed in recent years for which equipment components are commercially available. These methods are summarized in the following sections:

TECHNIQUES

Chronopotentiometry

Chronopotentiometry is a controlled current technique in which the electrolysis of an analyte occurs at a stationary electrode in a quiescent solution. The cell current is suddenly stepped to some fixed value and the resulting working

electrode potential is displayed against time. The fundamental equation for chronopotentiometry is the Sand equation:

$$\tau^{1/2} = \frac{\pi^{1/2} FAnD^{1/2} C^b}{2i} \qquad (1)$$

where τ, F, A, i, n, D and C^b are the transition time (sec), the Faraday (96,490), the area of the working electrode (cm^2), the constant current (μA), the number of electrons, the diffusion coefficient of the electroactive species (cm^2/sec), and bulk concentration of the latter ($moles/cm^3$), respectively.

The potential-time equation for an irreversible system is

$$E_w = \frac{RT}{\alpha n_a F} \left\{ \ln (nFAC^b k_c) + \ln \left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right] \right\} \qquad (2)$$

where

E_w = potential of the working electrode.

The kinetic factors (k_c or k_a) and αn_a can be derived from a chronopotentiogram using the above Equation (2).

Chronoamperometry

In chronoamperometry, the potential of the working electrode is suddenly stepped to some fixed value and the electrolysis current is displayed against time. Diffusion is the sole mode of mass transport, and the resulting current is

given by the Cottrell equation:

$$i_d = \frac{nFAD^{\frac{1}{2}}C^b}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}} \qquad (3)$$

where t is time (in seconds) after the controlled potential has been applied to the working electrode.

If the electrolysis current is not diffusion-controlled (which is often the case with an irreversible system) the resulting current is given by

$$i = i_d \left[\pi^{\frac{1}{2}} \lambda e^{\lambda^2} \operatorname{erfc}(\lambda)\right] \qquad (4)$$

where

$$\lambda = k_C \frac{t^{\frac{1}{2}}}{D^{\frac{1}{2}}} \qquad (5)$$

and

$$\operatorname{erfc}(\lambda) = 1 - \frac{2}{\pi^{\frac{1}{2}}} \int_0^{\lambda} e^{-z^2} dz \qquad (6)$$

From Equation (4), we see that k_C (or k_a) can be calculated from any applied potential by selecting current-time values from the chronoamperogram. The expression in Equation (6) is called the error function of λ. The value of $\operatorname{erfc}(\lambda)$ depends only on λ. The integral is evaluated numerically and can be found in standard tables.

Linear Potential Sweep Voltammetry

This technique involves scanning the working electrode potential linearly at a rapid rate (several mV/sec to several

hundred mV/sec). Cyclic voltammetry is an extension of the potential sweep technique in which the potential is swept back and forth over the same region several times. The principle governing this technique is explained later in this report.

Differential Pulse Voltammetry

This technique consists of superimposing a fixed-height potential pulse at regular intervals on the slowly varying potential associated with dc polarography. The current is sampled twice during each operating interval and the difference between these two samples is presented to the output of the amplifying system in the form of a peak. The current difference is proportional to concentration of the electroactive material.

Chronocoulometry

This is relatively a new technique and involves current-time integration of the Cottrell equation for chronoamperometry (Equation 3). A charge-time relationship results and is given by

$$Q = 2\, nFC_{ox}^{b}\, (D_{ox}t/\pi)^{\frac{1}{2}} \qquad (7)$$

where Q = charge in coulombs. Thus a diffusion-controlled chronocoulometric response exhibits a Q vs $t^{1/2}$ proportionality. In the event of adsorption, the Q vs $t^{1/2}$ plots should

yield positive intercepts on the Q axis for potential steps that are sufficiently large.

PREVIOUS STUDIES

Results of the examination of aliphatic amines have been reported by Mann[3]. He showed that the ease of oxidizability is:

tertiary > secondary > primary

Other workers have also investigated the oxidation of aliphatic[4,5,6] and aromatic[7,8] amines at stationary electrodes by potential sweep cyclic voltammetry. Most of these reports have been concerned with elucidation of the reaction mechanism in non-aqueous solvents such as acetonitrile and dimethylsulfoxide and very few, if any, have dealt with the analytical application of this technique to the determination of amines and sulfides. Drushell and Miller[9] have studied anodic polarographic estimation of aliphatic sulfides in petroleum, and oxidation of sulfur compounds, notably cysteine, was investigated by Davis and Bianco[10]. Also, Nicholson[11] has reported on the oxidation of aliphatic and aromatic sulfides. We have applied the techniques of linear potential sweep cyclic voltammetry and chronocoulometry to the studies of anodic oxidation of amines and sulfides.

EXPERIMENTAL

Cyclic voltammograms were obtained by the use of a Tacussel Potentiostat Type PRT 20-2. The current was determined by measuring the voltage drop across a precision resistor in series with the working electrode. Current-voltage curves were recorded using a Tektronix 5103N storage oscilloscope with a Type 5B10N plug-in time base. When the voltammogram was satisfactory, a photograph was taken with a Type C-5 Polaroid camera. The linear potential sweep was initiated by a triangular voltage function generated by a Wavetek Type 134 function generator, with a DC voltage offset capability. A flow diagram for current measurement is shown in Fig. 1. The 50Ω terminator on the output of the function generator ensures a maximum of 10V P-P amptitude for any given wave form.

All electrochemical experiments were performed in a water-jacketed all-glass cell of about 125 ml capacity with a five-hole Teflon cap. The working electrode was a Beckman #39273 platinum bottom electrode and the reference was a saturated calomel electrode.

For chronocoulometric experiments, the Tacussel potentiostat was used to apply the potential step. Current was sampled across a precision resistor connected to our own operational amplifier system utilizing Philbrick P85AU amplifiers. The iodine-iodide redox system was used to check the performance

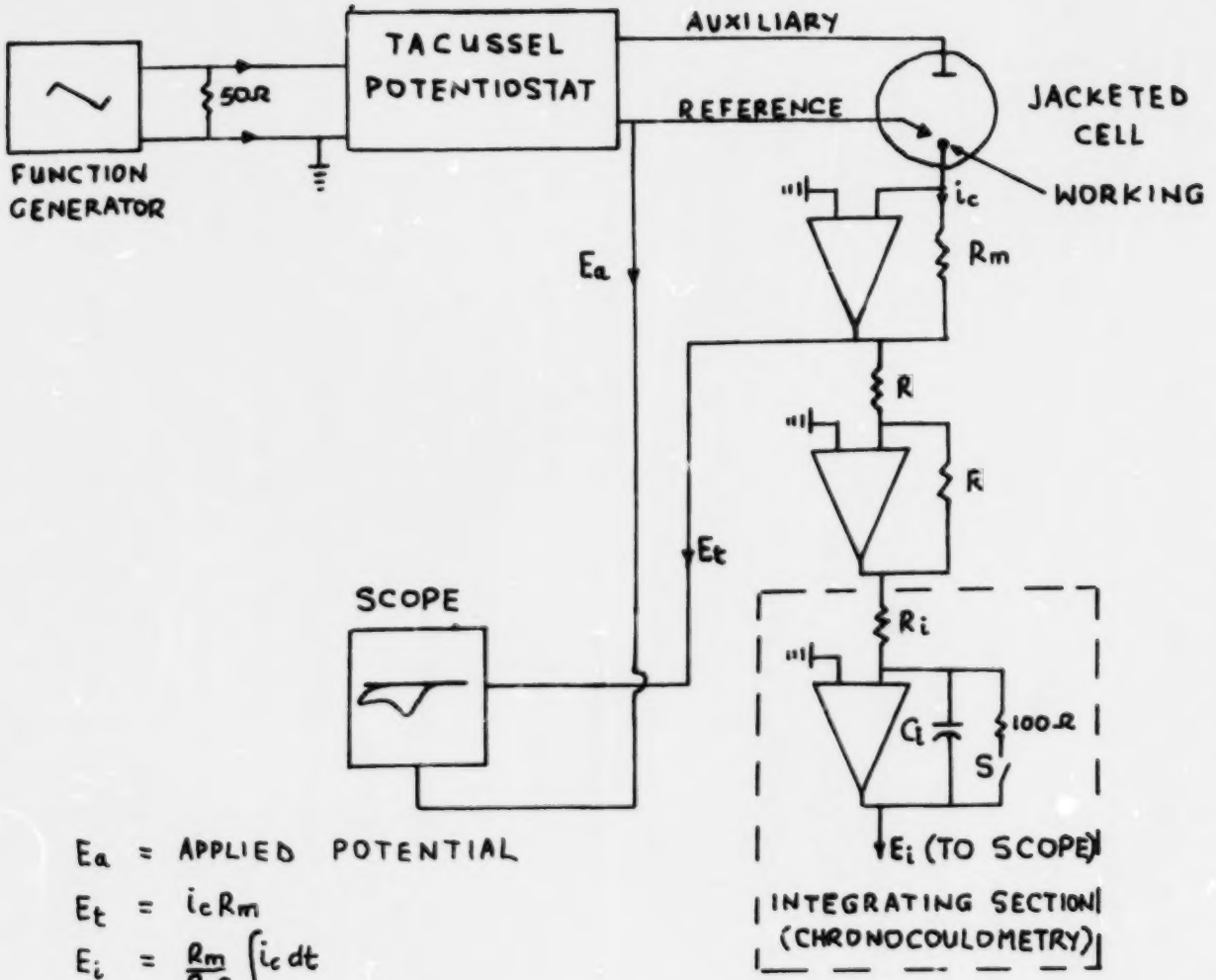

FIGURE 1. FLOW DIAGRAM FOR CURRENT MEASUREMENT.

of the method. The measuring cirucit is shown in Fig. 1. Switch S was thrown simultaneously with the intiation of the potential step. The resistors labelled R could be varied to achieve any desired amplification when solutions containing low concentrations of electroactive materials were being analyzed.

Reagents and Solutions

Reagent grade chemicals were purified by distillation. The solvent, acetonitrile, was purified by refluxing for 48 hrs over P_2O_5 and then distilling over K_2CO_3. The supporting electrolytes, $NaClO_4$, Et_4NClO_4 and Et_4NBF_4 were purified by recrystallization from suitable solvents.

Millimolar solutions of the amines and sulfides were prepared by introducing calculated volumes into 25 ml of acetonitrile containing 0.1 M concentrations of the appropriate supporting electrolyte. More dilute solutions were prepared by dilution.

The experimental procedure consisted of recording a voltammogram of a blank containing no amine or sulfide, and then recording another voltammogram in the presence of a calculated amount of the odorant compound. The analyte solution was deoxygenated with purified nitrogen for about 10 minutes before each measurement. Current integrals were similarly recorded on a blank before the introduction of the analyte of interest.

RESULTS AND DISCUSSION

The cyclic voltammogram of a 5×10^{-3} M solution of o-dianisidine in 1 M H_2SO_4, taken on a platinum electrode, is shown in Fig. 2. The sweep rate was 2.5 V/min and the ratio of anodic to cathodic current was unity, indicating a reversible system. This agrees with published data and suggests that our measuring system is functioning normally. The peak potential was 0.61 V vs saturated calomel electrode (SCE). Chronocoulometric analysis of the iodine-iodide system gave results that agreed with those of Christie and his co-workers[12].

Oxidation of Amines

The peak potentials obtained for the amines investigated are shown in Table I. The data were obtained using a sweep rate

Table I

Peak Potentials for some Odorous Amines at 5.3 V/min sweep rate

Compound	Peak Potential (Volts)	Concentration (millimolar)
n-butylamine	1.24	2.0
benzylamine	1.44	1.84
diethylamine	1.02	1.95
triethylamine	0.93	1.43

of 5.3 V/min at the given concentrations. The indicating electrode was an unshielded Pt-electrode in acetonitrile, 0.1 M in

$NaClO_4$. Each measurement was made on a clean electrode surface. The cyclic voltammograms for n-butylamine, benzylamine, diethylamine, and triethylamine are shown in Figures 3, 4, 5, and 6 respectively. We observe from the Figures and Table I, that the ease of oxidizability is:

triethylamine > diethylamine > n-butylamine > benzylamine

This order is in perfect agreement with the results of Mann[3]

Results for runs conducted with a mixture of (a) n-butylamine + diethylamine, (b) n-butylamine + triethylamine, and (c) n-butylamine + diethylamine + triethylamine are shown in Figures 7, 8, and 9 respectively. What is very significant in these voltammograms is that separate current peaks are not obtained for a mixture of these amines using linear potential sweep voltammetry at 5.3 V/min. Instead, a composite peak is obtained for any given mixture. For a mixture of primary, secondary, and tertiary amines a single peak appears at 1.09 V vs standard calomel electrode. This is about the average of the individual peak potentials obtained separately for the amines. The mixture of primary and secondary amines had a peak at 1.29 V vs standard calomel electrode and a peak at 0.97 V was obtained for the mixture of primary and tertiary amines. Thus, linear potential sweep voltammetry under these conditions appears to be incapable of differentiating among different amines, probably because of the proximity of the individual

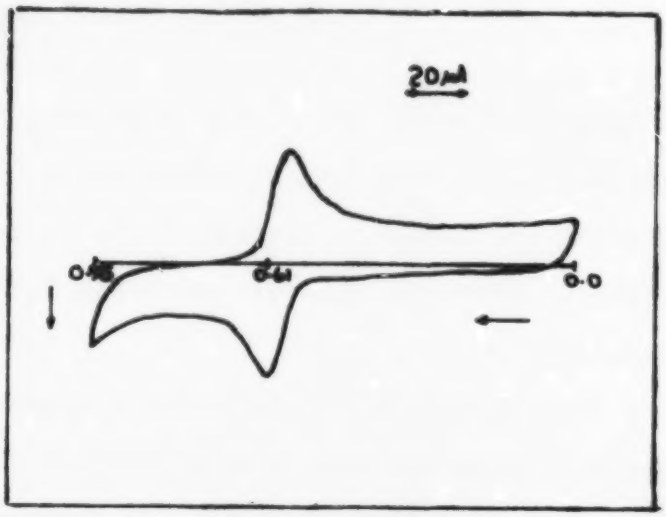

FIGURE 2. CYCLIC VOLTAMMOGRAM OF O-DIANISIDINE IN 1M H_2SO_4; CONCENTRATION, 5mM Pt-ELECTRODE

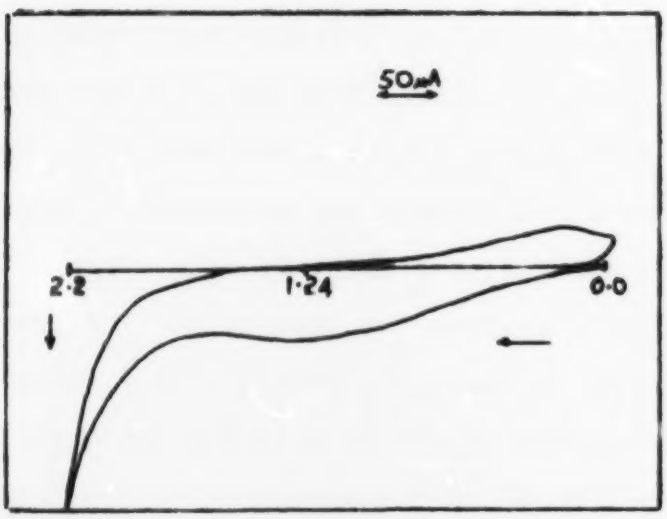

FIGURE 3. CYCLIC VOLTAMMOGRAM FOR 2mM n-BUTYLAMINE IN ACETONITRILE, 0.1M IN $NaClO_4$. SWEEP RATE 5.3 V/min. Pt-ELECTRODE

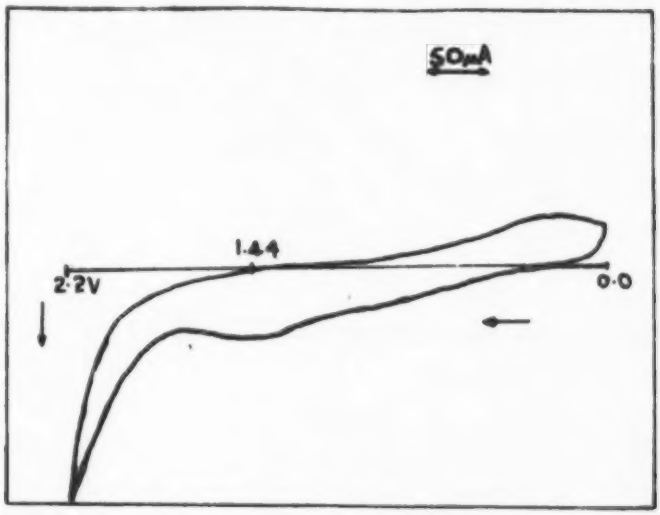

FIGURE 4. CYCLIC VOLTAMMOGRAM FOR 1.84 mM SOLUTION OF BENZYLAMINE IN ACETONITRILE, 0.1M IN $NaClO_4$. SWEEP RATE 5.3 V/min Pt-ELECTRODE.

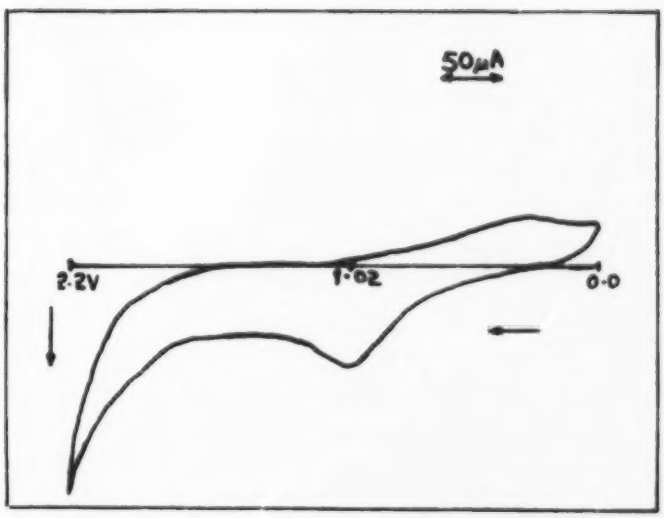

FIGURE 5. CYCLIC VOLTAMMOGRAM FOR 1.95 mM SOLUTION OF DIETHYLAMINE IN ACETONITRILE 0.1M IN $NaClO_4$. SWEEP RATE 5.3 V/min. Pt-ELECTRODE.

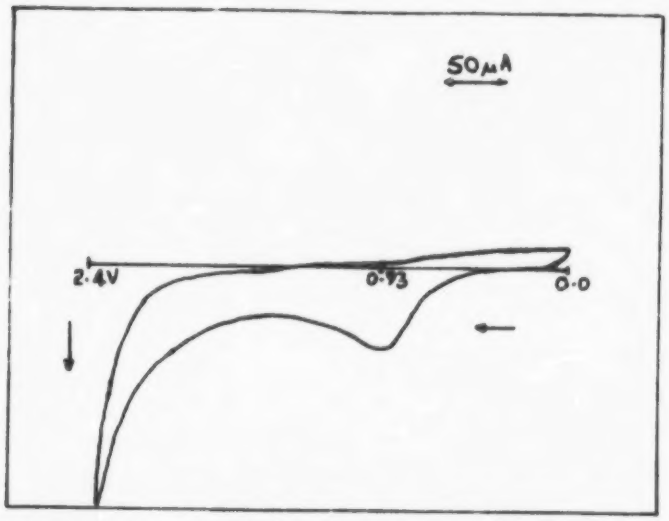

FIGURE 6. CYCLIC VOLTAMMOGRAM FOR 1.43 mM SOLUTION OF TRIETHYLAMINE IN ACETONITRILE, 0.1M IN $NaClO_4$. SWEEP RATE 5.3 V/min; Pt-ELECTRODE.

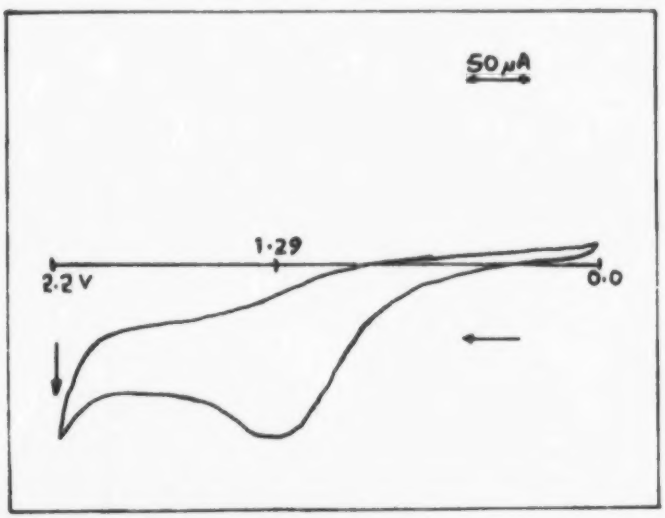

FIGURE 7. VOLTAMMOGRAM FOR A MIXTURE OF n-BUTYLAMINE AND DIETHYLAMINE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

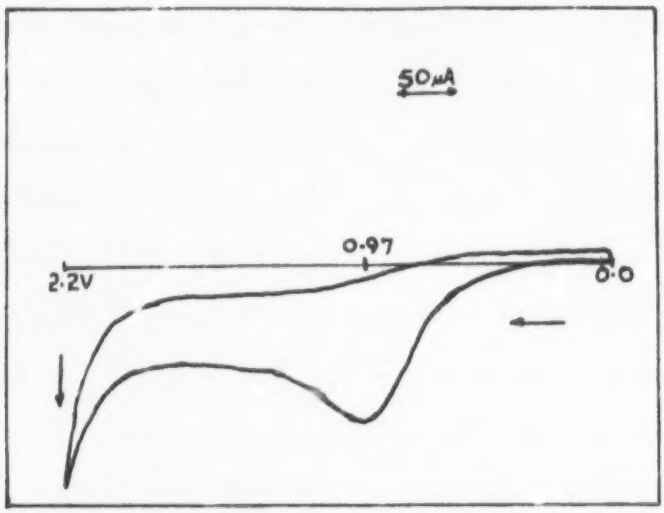

FIGURE 8. VOLTAMMOGRAM FOR A MIXTURE OF n-BUTYLAMINE AND TRIETHYLAMINE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

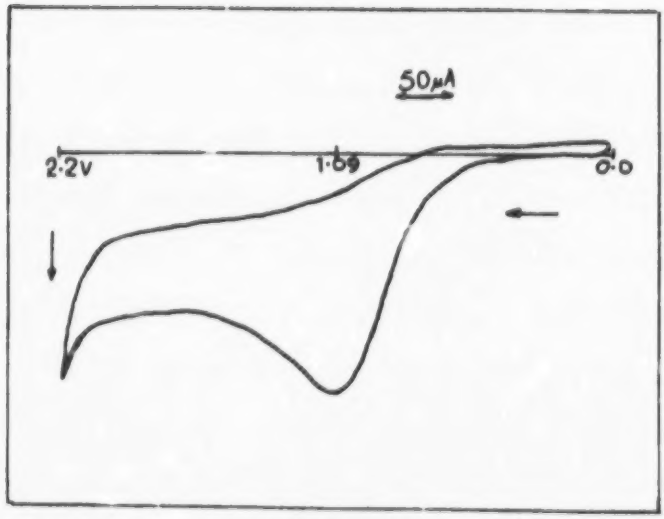

FIGURE 9. VOLTAMMOGRAM FOR A MIXTURE OF n-BUTYLAMINE, DIETHYLAMINE AND TRIETHYLAMINE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

oxidation potentials. However, it may be possible to analyze amines as a class and to differentiate them from other odorants.

All the voltammograms for the amines indicate that the oxidations are irreversible. Only anodic peaks were obtained, in contrast to the reversible oxidation of o-dianisidine shown in Fig. 2. The small cathodic peaks around 0.26 V vs standard calomel electrode in Figs. 3, 4, and 5 could be due to impurity in the amines or the supporting electrolyte. They are certainly not due to reduction of the oxidation product of the amines.

All the measurements were performed on platinum electrodes. A gold electrode appeared to be oxidized at potentials above 0.90 V and was therefore considered to be unsuitable. No clearly defined current peaks were observed on glassy carbon or on wax-impregnated graphite electrodes. The voltammogram obtained on glassy-carbon electrode for a mixture of n-butylamine, diethylamine, and triethylamine is shown in Fig. 10. This trace was obtained under the same experimental conditions as Fig. 9. The composite peak now appears at 1.23 V vs standard calomel electrode instead of 1.09 V vs standard calomel electrode as obtained in Fig. 9. Runs conducted on a carbon-paste electrode prepared according to the method of Marcoux et al.[13] showed well-defined voltammograms for amines. This electrode is therefore as good as platinum for oxidation of the chosen amines, and both are superior to glassy-carbon or wax-impregnated graphite electrodes.

Oxidation of Sulfides

Results for sulfides using a platinum electrode at a sweep rate of 5.3 V/min indicated that allyl sulfide, n-butylsulfide, and tert-butylsulfide could be oxidized on platinum in acetonitrile with 0.1 M $NaClO_4$ as supporting electrolyte.

Table II shows the peak potentials for the sulfides at the

Table II

Peak Potentials for some Odorous Sulfides at 5.3 V/min sweep rate

Compound	Peak Potential (Volts)	Concentration (millimolar)
Allyl sulfide	1.84	1.56
n-butylsulfide	1.78	1.15
t-butylsulfide	1.45	1.14

given concentrations. The voltammograms for the three sulfides are shown in Figures 11, 12, and 13 respectively. We observe that tert-butylsulfide is more readily oxidized than allyl sulfide and n-butyl sulfide, since it has the lowest peak potential. Comparison with triethylamine (Fig. 6), shows that the amine is more readily oxidized. The peak potentials are 0.93V and 1.45 V (vs standard calomel electrode) for the amine and sulfide respectively. The shoulder around 1.93 V in Fig. 13, for example, may be due to oxidation of the perchlorate ion, which is known to have a discharge potential of 2.10 V on a Pt-electrode in acetonitrile. A blank run on the solvent-

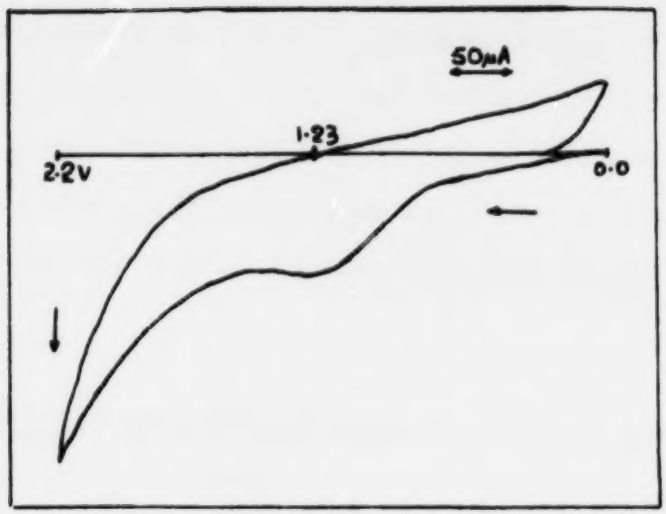

FIGURE 10. VOLTAMMOGRAM FOR A MIXTURE OF n-BUTYLAMINE, DIETHYLAMINE AND TRIETHYLAMINE ON GLASSY CARBON ELECTRODE. SWEEP RATE 5.3 V/min.

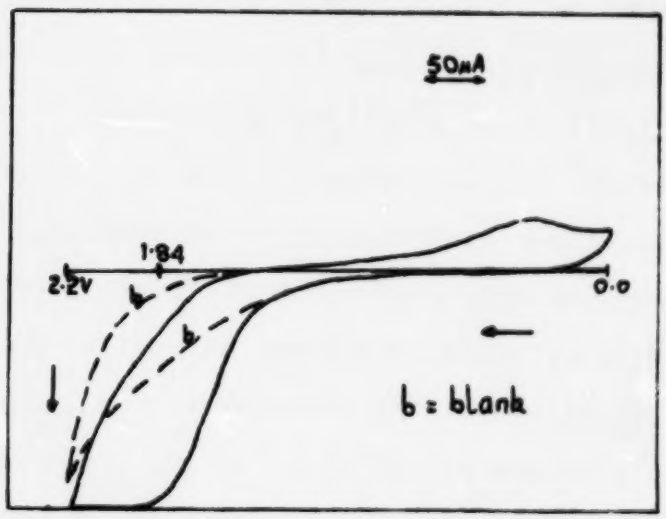

FIGURE 11. CYCLIC VOLTAMMOGRAM FOR ALLYL SULFIDE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

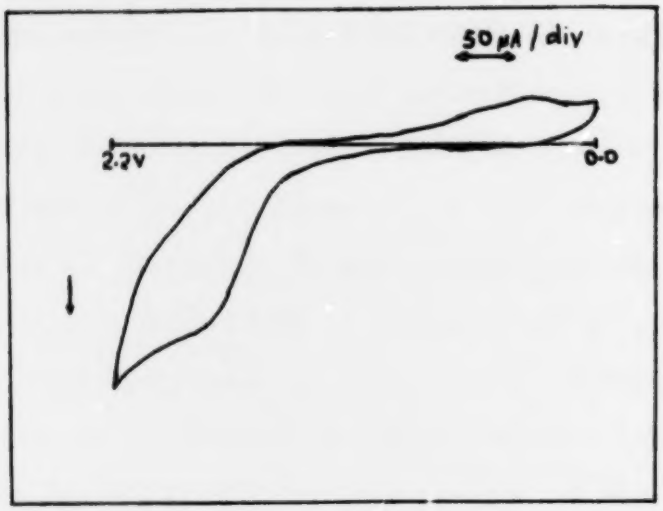

FIGURE 12. CYCLIC VOTAMMOGRAM FOR n-BUTYL SULFIDE ON Pt-ELECTORDE. SWEEP RATE 5.3 V/min.

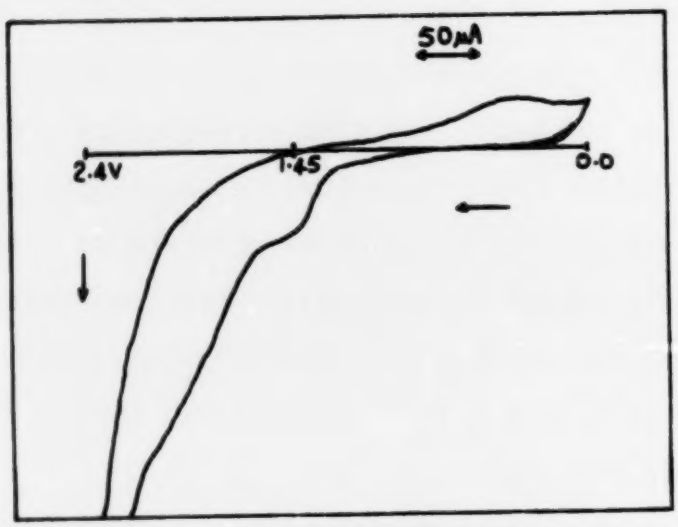

FIGURE 13. CYCLIC VOLTAMMOGRAM FOR t-BUTYL SULFIDE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

electrolyte system is shown in Figure 14. There is a shoulder at around 1.94 V, confirming that the perchlorate ion is being discharged at this potential. The oxidation of the solvent is indicated at around 2.20 V. A small cathodic peak is seen around 0.26 V and the appearance of this peak in previous runs is attributable to an impurity in the supporting electrolyte.

Runs conducted on a mixture of n-butylsulfide and tert-butylsulfide did not show clearly defined separate peaks. One peak was obtained at a potential of 1.72 V, which is more anodic than the potential at which tert-butylsulfide is oxidized. This is shown in Fig. 15. The cathodic peak has been attributed to an impurity in the supporting electrolyte.

Fig. 16 shows the voltammogram obtained for a mixture of n-butylsulfide, tert-butylsulfide, and triethylamine on a platinum electrode, at a sweep rate of 5.3 V/min. The voltammogram of Figure 17 is for a mixture of n-butylsulfide and tert-butylsulfide on one hand, and also n-butylamine and triethylamine on the other hand. What appears to be very significant is that a clear separation of peaks is observed for the oxidation of amines and sulfides respectively, when these are components of a mixture. The amine peak appears around 0.95 V and the sulfide peak at around 1.72 V. This gives a separation of 770 mV between the peaks.

It therefore appears possible to characterize a mixture of amines and sulfides by linear potential sweep voltammetry.

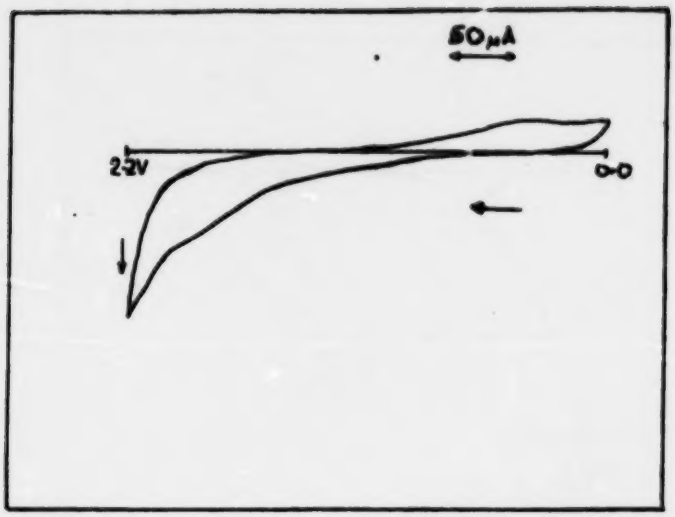

FIGURE 14. CYCLIC VOLTAMMOGRAM FOR SOLVENT-ELECTROLYTE SYSTEM ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

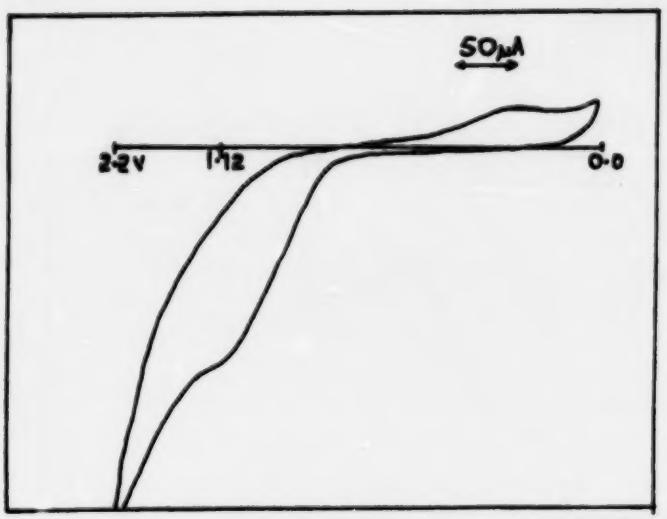

FIGURE 15. VOLTAMMOGRAM OF n-BUTYLSULFIDE AND t-BUTYLSULFIDE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

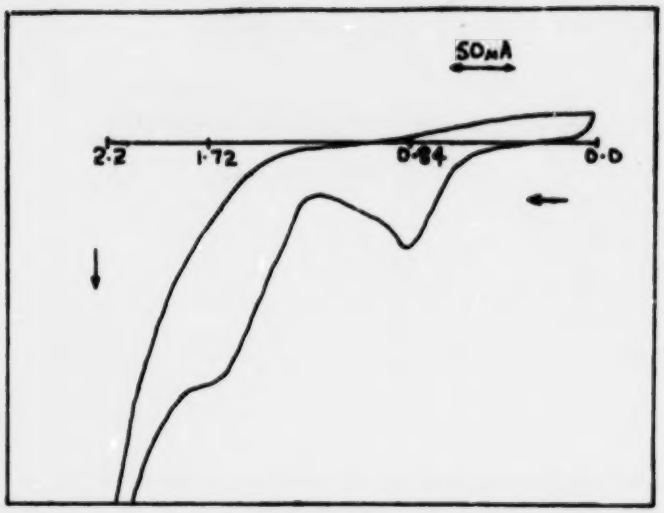

FIGURE 16. VOLTAMMOGRAM OF A MIXTURE OF n-BUTYLSULFIDE, TERT-BUTYLSULFIDE AND TRIETHYLAMINE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

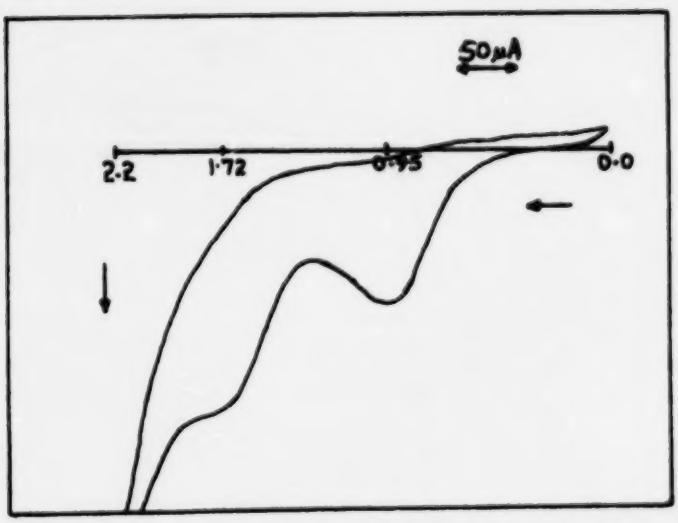

FIGURE 17. CYCLIC VOLTAMMOGRAM OF A MIXTURE CONTAINING n-BUTYLSULFIDE, t-BUTYLSULFIDE, n-BUTYLAMINE AND TRIETHYLAMINE. RUN CONDUCTED ON Pt-ELECTRODE AT 5.3 V/min.

Quantitative determination would thereafter be effected by controlled potential voltammetry. This is a matter for future work.

The amines are generally more readily oxidized than the sulfides. Oxidation of a mixture of amines only would be expected to occur around 1.0 V while a mixture containing only sulfides is expected to oxidize above 1.72 V, at a given sweep rate, say 5.3 V/min. The position of the peak could be directly related to any specific amine or sulfide. This would, of course, require calibration of the measurement apparatus with known odorous compounds, in terms of peak potentials. For example, in Fig. 18 we have the voltammogram of a mixture of triethylamine and t-butylsulfide. Peak potentials appear at 0.800 V and 1.43 V, and these closely approximate to the values obtained when these compounds were measured separately, as shown in Tables I and II. For a mixture containing t-butylsulfide, diethylamine, and triethylamine, there is a shift of the amine peak towards a more anodic value of 0.86 V but the sulfide peak still appears at 1.43 V. This is illustrated in Fig. 19.

Voltammograms obtained using a carbon-paste electrode, prepared as previously indicated, showed that this electrode is superior to the platinum electrode in the anodic oxidation of sulfides. The anodic waves were better defined and are more suited for quantitative analyses. Also, for the same geometric

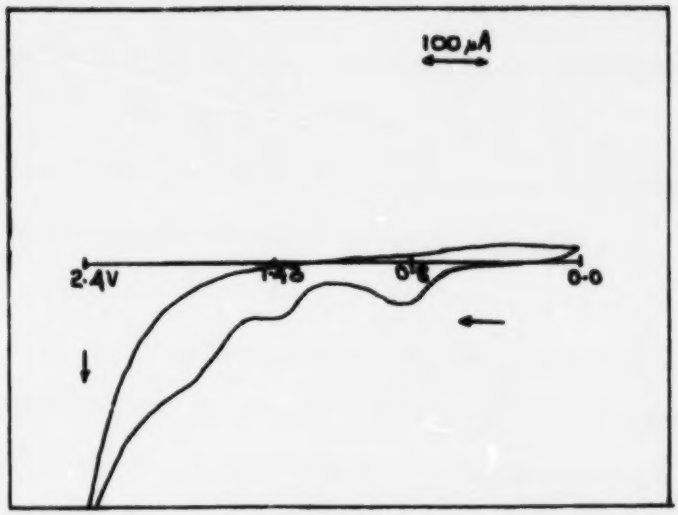

FIGURE 18. VOLTAMMOGRAM OF t-BUTYLSULFIDE AND TRIETHYLAMINE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min. THE SENSITIVITY HERE IS HALF THAT OF FIGURE 17.

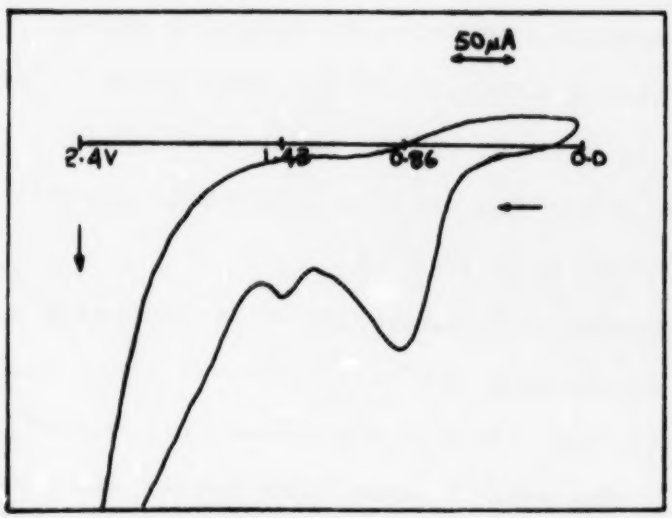

FIGURE 19. VOLTAMMOGRAM OF TERT-BUTYLSULFIDE, DIETHYLAMINE AND TRIETHYLAMINE ON Pt-ELECTRODE. SWEEP RATE 5.3 V/min.

area of working electrodes, carbon-paste gives greater current density for a fixed concentration of analyte. In the oxidation of allyl sulfide, it was noticed that filming occurred on a platinum electrode but was negligible on a carbon-paste electrode. The evidence for filming was non-reproducibility of current upon repetitive sampling on the same surface.

Effects of Variation of Supporting Electrolyte

Variation in supporting electrolyte causes appreciable changes in the shape of the current-time curves during oxidation of amines and sulfides. For example, oxidation of allyl sulfide on carbon-paste in acetonitrile with 0.1 M Et_4NBF_4 as supporting electrolyte, did not give any well-defined peak. Results obtained with other odorants, such as thiophenol, benzylmercaptan, t-butylsulfide, and some amines, showed that perchlorates are generally preferred to the tetrafluoroborates as supporting electrolytes.

In fact, it has been postulated[14] that the reaction potential is subject to variations with change in electrolyte because of alteration of the liquid junction potential involved in the reference probe. In addition, variation in the supporting electrolyte may alter the double layer at the electrode-solution interface enough to cause significant variation in reaction rate and hence in the shape of the current-time curve.

An Approach to Quantitative Analysis

In linear sweep peak voltammetry, the current-potential curve exhibits a maximum or peak and the current is given by

$$i_p = kn^{\frac{3}{2}} AD^{\frac{1}{2}} C^b v^{\frac{1}{2}}$$

where i_p = peak current, amperes

A = area of electrode, cm^2

V = rate of potential change, volts/sec

k = a constant, called the Randles-Sevcik constant

D = diffusion coefficient of the electroactive species, cm^2/sec

C^b = bulk concentration of the electroactive material, moles/ml

and n = number of electrons transferred in the reaction.

The value of i_p is therefore seen to be directly proportional to concentration and the sweep rate. The curves may be characterized by the peak potentials E_p, as we have shown above in the oxidation of amines and sulfides, or by the half-wave potential, $E_{p/2}$. The above equation strictly holds for a rapid charge-transfer (reversible) process, but we have seen from the voltammograms of the amines and sulfides that their reactions on a platinum electrode are irreversible.

In chronocoulometric analysis, a charge-time relationship obtains, and is given by $Q = 2nFAC^b(Dt/\pi)^{1/2}$, where Q is the

charge (coulombs), n is the number of electrons, F is the Faraday (96,490 coulombs), and t is the time (sec). Thus a diffusion-controlled chronocoulometric response exhibits a Q vs $t^{1/2}$ proportionality. It is also seen that Q is directly proportional to concentration for a given t.

We have therefore examined the applicability of the cyclic voltammetric and chronocoulometric equations to the quantitative determination of amines and sulfides. The chronocoulometric investigation has attempted to correlate total charge at a given time with bulk concentration of amines and sulfides.

The dependence of peak current on concentration and sweep rate respectively, was examined using triethylamine. A plot of current against the square root of the sweep rate was linear, as shown in Fig. 20. The concentration of triethylamine was 5.7×10^{-3} M in acetonitrile solution, 0.1 M in $NaClO_4$. The currents were highly reproducible at a given sweep rate.

Figure 21 shows a plot of current against concentration at a sweep rate of 9.6 V/min. There appears to be a deviation from linearity at concentrations greater than 5 millimolar. This is probably due to uncompensated IR drop which increases with increasing concentration. Because of this, the potential of the working electrode is not exactly equal to the applied potential, and the measured current is below the theoretical

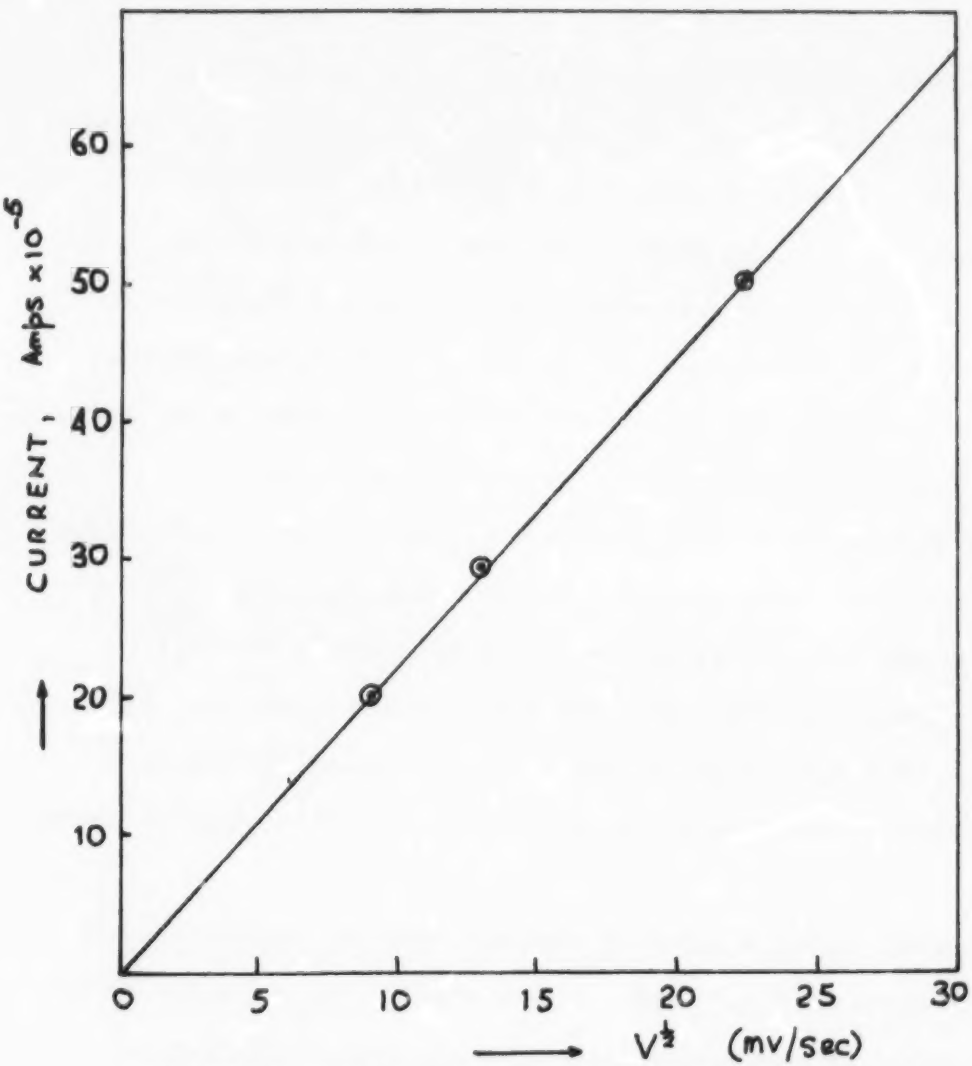

FIGURE 20. PLOT OF CURRENT VS SWEEP RATE FOR OXIDATION OF 5.7 X 10^{-3M} TRIETHYLAMINE ON Pt-ELECTRODE.

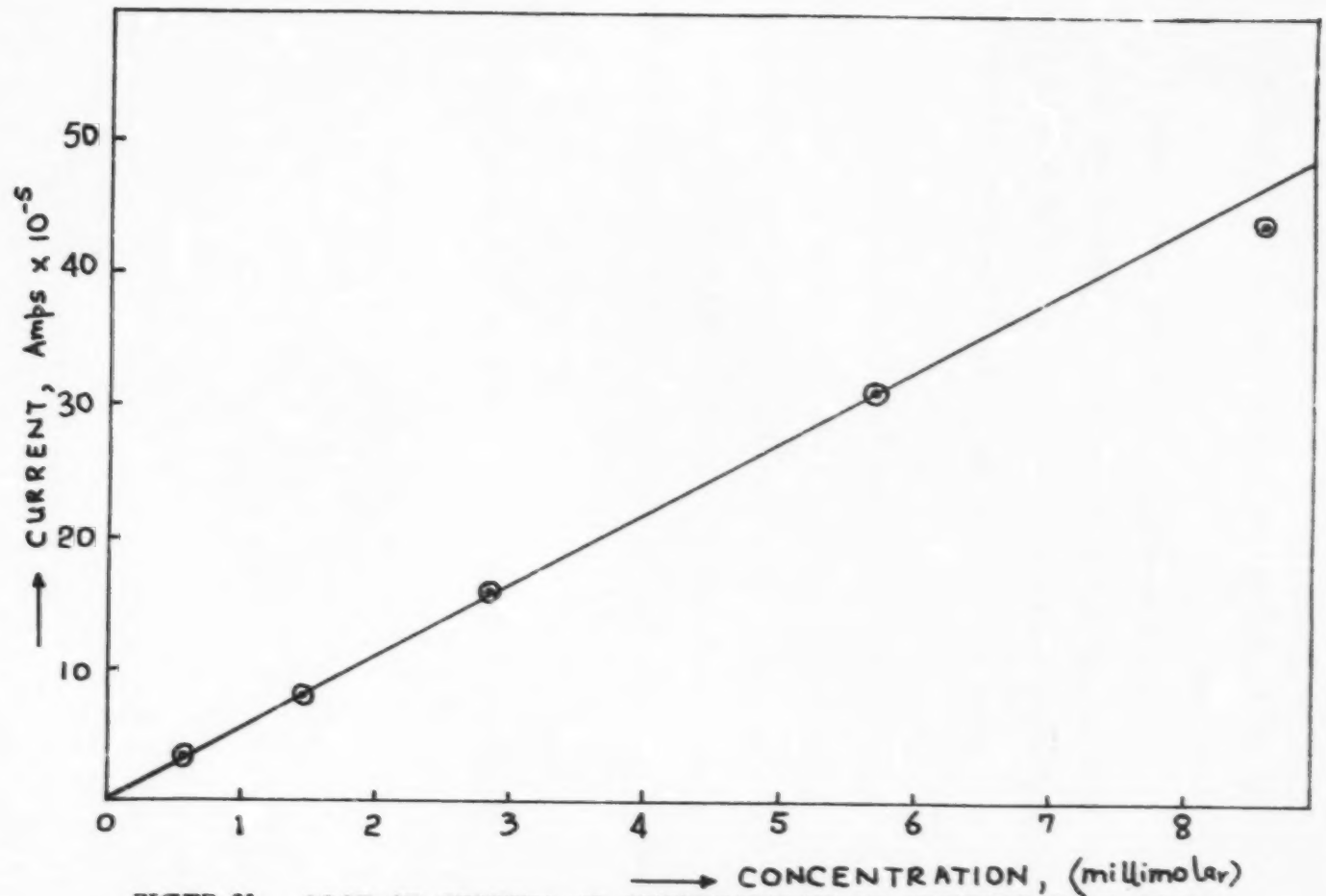

FIGURE 21. PLOT OF CURRENT VS CONCENTRATION OF TRIETHYLAMINE USING Pt-ELECTRODE. SWEEP RATE, 9.6 V/min.

value. The observed displacement of the peak potential towards more anodic values with increasing concentration is consistent with the above reasoning.

The range of current linearity at low concentrations offers promise that potential sweep peak voltammetry may be applied to quantitative analysis. Sensitivity could be improved by increasing the sweep rate, with due electronic compensation for the background current.

Identical results were obtained for n-butylamine and diethylamine. When a mixture of amines was analyzed, the total current obtained was equal to the sum of the currents obtained when the amines were separately analyzed. These findings are shown in Table III. The total current for a mixture of amines

Table III

Oxidation of Amines on Pt-electrode, Sweep Rate 9.6 V/min

Composition of solution	Concentration µl/50 ml CH_3CN	Current, µA
Diethylamine	10	80
Triethylamine	10	80
Diethylamine	40	305
Diethylamine + triethylamine	10 of each amine	160
Diethylamine + triethylamine	40 of diethylamine + 10 of triethylamine	370

is therefore directly proportional to their overall concentration.

The current value obtained for a mixture of 40 µl of diethylamine and 10 µl of triethylamine in 50 ml of solution is less than the sum of the currents obtained when corresponding concentrations of the amines were analyzed separately (see Table III). This difference would be due to preferential adsorption of one component or to uncompensated IR drop which leads to a decrease in current with increasing concentration (Fig. 21).

Analyses of sulfides indicated current reproducibility for n-butylsulfide and t-butylsulfide but not for allyl sulfide. Our observation was based on consecutive runs on the same surface of a platinum electrode. No such decrease occurred, however, when a carbon-paste electrode was used. It would appear that adsorption of allyl sulfide, or one of its oxidation products, is responsible for this pronounced decrease in current when platinum electrode is used. The magnitude of this phenomenon is illustrated in Fig. 22, which is a voltammogram of allyl sulfide taken after three consecutive runs on a platinum electrode. The current has decreased from an initial value of 210 µA (Fig. 11), to 110 µA. Peak (b) of the latter figure was obtained on a second sweep of the 3rd run. The cause of this and similar phenomena will be investigated, since its elimination is essential to the design of an

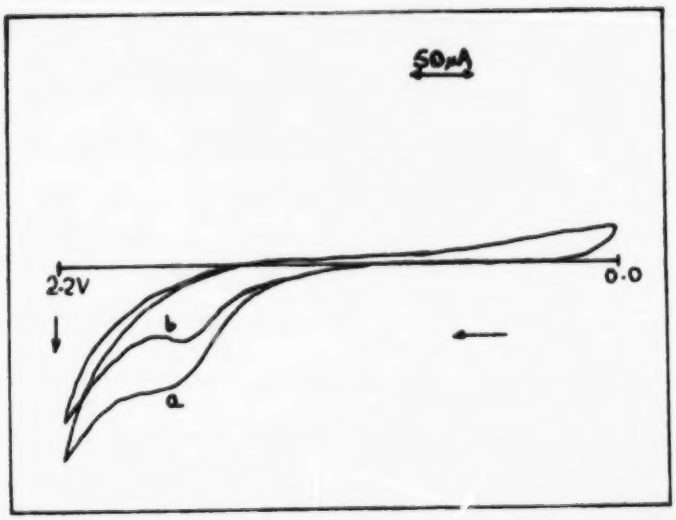

FIGURE 22. VOLTAMMOGRAM FOR THE OXIDATION OF ALLYL SULFIDE ON Pt-ELECTRODE AFTER 3 CONSECUTIVE RUNS. SWEEP RATE 5.3 V/min.

instrument for quantitative determination of sulfides. Irreversible dimerization of allyl radical-ion to disulfides (resulting from the one-electron oxidation of allyl sulfide) might take place, giving rise to an insoluble film on the electrode surface. Such dimerization does not occur with n-butylsulfide or with t-butylsulfide, possibly because of steric hindrance.

Oxidations of sulfides on gold and glassy-carbon electrodes did not reveal any significant advantage over platinum electrodes. The current peaks were not clearly defined.

Chronocoulometric runs with different concentrations of triethylamine on a Pt electrode in acetonitrile, 0.1 M in $NaClO_4$ as supporting electrolyte, are shown in Fig. 23. The potential was stepped from 500 to 1400 mV. Although a linear relationship exists between charge and $t^{1/2}$, we did not obtain a direct proportionality between charge and concentration at a given time. For a time of 1 sec, the total charge was 200, 480, and 1040 μC for solutions containing 5, 10, and 20 μl of triethylamine respectively, in 25 ml of acetonitrile.

The non-proportionality of charge to concentration could be due to adsorption effects, which are apparent from Fig. 23. In the event of adsorption, the Q vs $t^{1/2}$ plots should yield positive intercepts on the Q axis at zero time for potential steps that are sufficiently large. Such intercepts were obtained, after due compensation for double-layer capacitive

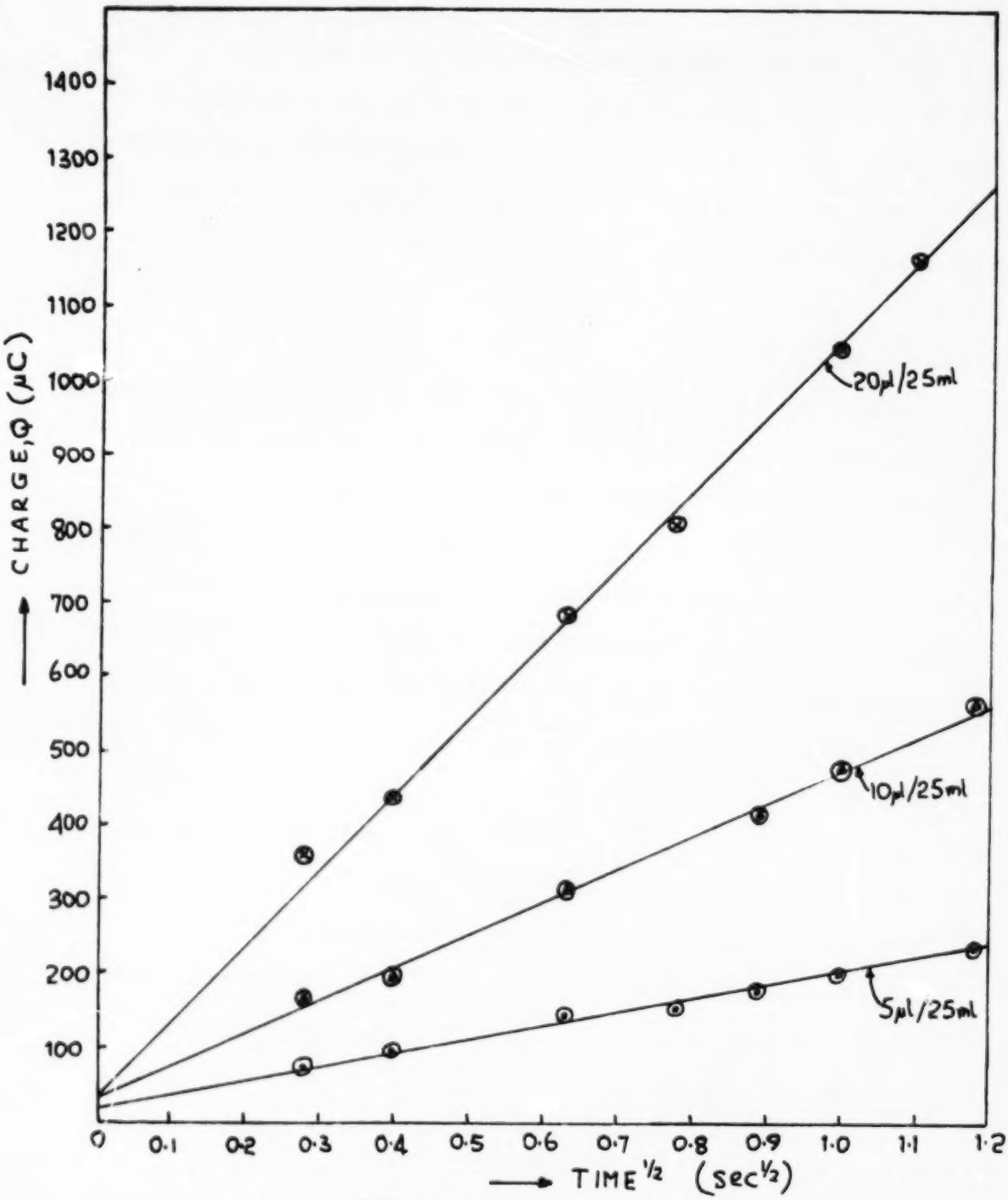

FIGURE 23. Q VS $t^{1/2}$ PLOT FOR VARIOUS CONCENTRATIONS OF TRIETHYLAMINE; POTENTIAL STEP FROM 500mV TO 1400mV.

charge. The adsorption effects are maximal at high concentrations and will make the chronocoulometric response non-diffusion controlled. Hence Q would be expected to increase out of proportion to bulk concentration as observed.

CONCLUSIONS

We have attempted the qualitative and quantitative characterization of amines, sulfides, and their mixtures. It is significant that a clear separation of peaks is observed for the oxidation of amines and sulfides respectively, when these are components of a mixture, using the technique of linear potential sweep cyclic voltammetry. An attempt to relate total charge to bulk concentration of analyte using chronocoulometry indicated that adsorption effects could be important at higher concentrations.

The next phase of this investigation will involve authentic samples from several industrial odor sources. We are hopeful that a combined cyclic voltammetric and chronocoulometric technique could be applied to the instrumental analysis of odorous amines and sulfides.

ACKNOWLEDGMENT

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